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Exhibit A

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PREPARATION AND PROPERTIES OF CANDIDATE POLYAMIDE RESINS FOR TESTING IN SOLVENT JET INKS

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SUMMARY AND CONCLUSIONS

Polyamide resins similar in composition and properties to those currently sold by Arizona as flexographic ink resins are potentially useful in formulating digital ink-jet inks. The solvents currently used in these inks differ from flexo ink solvents in that they are less volatile (high flash points). Arizona has little solubility data for dimer polyamides in these solvents, especially polyethylene glycol ethers and acetates.

To obtain this data for a variety of polyamides and to select materials for further testing as jet ink resins, we prepared polyamides from many of the commercially available diamines, all having 20% termination with either tall oil fatty acid (UNITOL®BKS) or propionic acid, adjusting the softening point and hardness of a particular diamine-based composition by the relative amounts of dimer acid and a short-chain diacid, and testing solubility of the more promising materials in n-octanol, ethyl lactate, and cyclohexanone. None were soluble in tripropylene glycol methyl ether, DuPont's dibasic acid ester blend, or ethoxy ethyl propionate.

The following diamines are candidates for further development:

- Ethylene diamine/hexamethylene diamine mixture
- Bis(4-aminocyclohexyl) methane
- 1,2-Diaminocyclohexane
- Bis(aminopropyl) piperazine
- Isophorone diamine
- Trimethylhexamethylene diamine
- Jeffamine D-400/D-230 mixture
- Dimer diamine

The following diamines did not produce resins suitable for further testing:

- meta-Xylene Diamine
- Piperazine
- Huntsman XTJ-504 (formerly EDR-148)
- Jeffamine D-2000

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BACKGROUND

The central technical challenge for Project P-011897, Solvent-Based Jet Ink Resins, is to identify a resin for use in an organic solvent-based ink which will allow customers of digital imaging equipment such as Markem, Gretag (Rastergraphics), and NUR to produce images with better color, adhesion, and abrasion-resistance on vinyls used now in outdoor displays and other substrates, such as polyethylene, which are of growing interest. Jerry King, Phil Johnson, Stephen Bush and I have laboratory work underway to prepare and test resins for potential use in these applications.

One working hypothesis is that a dimer acid-based polyamide will perform well. Our reasoning is straight-forward; because substrates and ink properties for digital printing are similar to those for flexographic printing, resins similar to those which set the standard for performance in solvent flexographic printing inks worldwide should be useful as well in solvent digital printing inks.

Neutral (low acid and amine number) low molecular weight dimer polyamides are clear and hard, can be brittle or flexible, have good adhesion to many substrates and are readily soluble in fatty alcohols such as butanol but are not soluble in toluene, acetone, THF, ethyl acetate or mineral oils. That polyamides are not currently used to formulate digital inks is likely due to the lack of familiarity of jet ink makers with these resins and their poor solubility in the solvents currently used to formulate these inks such as ether acetates and ether alcohols. This dictated our program approach, to attempt first to prepare a polyamide having solubility in the latter solvents. Second, to prepare a wide variety of polyamide resins without regard to their solubility properties but then identify a solvent (single component or blend) that might be acceptable to the digital ink industry and would dissolve the best candidate resins.

This report discusses the preparation, properties and solubility test results of a variety of candidate polyamides. Poly(ester-amides) and polyurethanes will be the subjects of a separate report.

RESIN COMPOSITION SELECTION

To keep the number of polyamide preparations manageable we selected compositions most likely to meet two performance criteria: low solution viscosity and low tack (which should mean good dry rate and block resistance). In practice we did not measure these properties for screening work but simply set the resin molecular weight (and thus the approximate solution viscosity) by using a termination level of approximately 20 eq.% for each resin. We adjusted resin compositions of each "family" (see below) to obtain materials non-tacky at room temperature (if possible). Commercial formulations, previous synthetic work of Dan Rumack (Princeton R&D), and recent work I carried out served as a guide to selecting formulations. As possible feedstocks, we have many commercially available diacids and diamines (TABLE 1).

TABLE 1. Representative Commercially Available Diacids and Diamines

DIACID	Abbrev-iation	Equivalent Weight		DIAMINE	Abbrev-iation	Equivalent Weight
Adipic	ADP	73.1		Ethylene Diamine	EDA	30.05
Isophthalic	IPA	83.1		1,2-Diaminopropane	DAP	37.05
Terephthalic	TPA	83.1		Piperazine	PIP	43.1
1,4-Cyclohexane	CHDA	86.1		1,2-Diaminocyclohexane	DACH	57.1
Azeleic	AZL	95		Hexamethylene Diamine	HMDA	58.0
Sebacic	SEB	101.1		Dytek A	MPMDA	58.6
Dodecanedioic	DOD	115.2		meta-Xylene Diamine	XDA	68.0
Fumaric Acid	FUM	116		Huntsman XTJ-504	XTJ504	74.0
Westvaco 1550	C21	207		Trimethylhexamethylene	TMHMDA	79.1
Dimer Acid	D14	288		Bis(aminopropyl) Piperazine	BAPP	100
				Isophorone Diamine	IPDA	101
				Bis(aminocyclohexyl) Methane	PACM	105
				Jeffamine D-230	D230	119
				Jeffamine D-400	D400	210
				Versamine 551 Dimer Diamine	V551	285
				Jeffamine D-2000	D2000	1000

To keep the initial screening manageable, we followed these guidelines:

- Used a single diamine. This study is, essentially, a search for the most promising diamines to use to build a polyamide. I note and discuss a few exceptions.
- Used adipic acid, treating as essentially equivalent all four of the short-chain linear diacids (SCDA); adipic = azeleic = sebacic = dodecanedioic acid. If a polyamide containing a high content of one of these proved itself an outstanding candidate resin, we could always make the others and look for an optimal resin. Again, I note when I broke this guideline and discuss why.
- Did not use any aromatic acids, as being relatively hard to react
- Did not use Westvaco-1550 C-21 diacid, itaconic acid, and fumaric acid.
- Used either propionic acid or UNITOL®BKS tall oil fatty acid as the terminating monoacid.
- Dimer acid in this work is Unidyme 14 unless otherwise noted.

I first made a polyamide with dimer acid as the only diacid for each diamine using 20% termination. If this polyamide was tacky and low in SP (lower than about 100°C), I made another candidate using a small amount (<40 eq.%) of SCDA. I continued this process, raising/lowering the SCDA content until the tack was reduced and the SP became acceptably high.

RESULTS

Ethylene and Hexamethylene Diamines

#0014-105-B	Weight %	Equivalent %	Acid Number	11.8
Unitol BKS	19.0%	20.0%	Amine Number	0.5
Unidyme 14	68.3%	71.4%	Softening Point	154.7
Sebacic Acid	2.9%	8.6%	Viscosity,150°C	n.d.
EDA	9.8%	98.6%	20% in n-Octanol	Clear Gel

#0014-123-A	Weight %	Equivalent %	Acid Number	5.3
Unitol BKS	18.2%	20.0%	Amine Number	0.9
Unidyme 14	65.3%	71.4%	Softening Point	111.3
Sebacic Acid	2.8%	8.6%	Viscosity,150°C	465 cP
HMDA	4.7%	49.1%	20% in n-Octanol	Soluble
EDA	9.1%	49.1%	20% Ethyl Lactate	2-Phase Gel

Arizona sells a variety of low molecular weight dimer acid polyamides into the flexographic ink market, for example, UNIREZ®2215, 2221, and 2218. All of these have propionic acid termination and all contain a blend of nearly equal equivalents EDA and HMDA with a small amount of diethylenetriamine. Termination levels are typically greater than 20%, for example, UNIREZ®2221 is 37% terminated, half as propionic acid and half as BKS.

We made a resin #0014-105-B using only EDA with a little sebacic acid to raise its SP (not adipic, since conventional resins do not contain the latter). Although it dissolved in hot n-octanol, the solution gelled when cool. This means it cannot be a candidate for further testing. Substitution of half of the EDA with HMDA overcomes this difficulty, although this resin is not soluble in ethyl lactate. "Benchmark" resin #0014-123-A, is clear, flexible, and non-tacky, properties we expect are advantageous for a digital printing ink resin.

Bis(4-aminocyclohexyl) Methane (PACM)

#0014-104-A	Weight %	Equivalent %	Acid Number	4.6
Unitol BKS	14.6%	20.0%	Amine Number	1.3
Unidyme 14	58.8%	80.0%	Softening Point	95
PACM	26.6%	99.0%	Viscosity,175°C	1455 cP
			20% in n-Octanol	Soluble

#0014-116-A	Weight %	Equivalent %	Acid Number	4.6
Unitol BKS	15.8%	20.0%	Amine Number	1.5
Unidyme 14	52.9%	66.7%	Softening Point	96.3
Adipic Acid	2.7%	13.3%	Viscosity,150°C	7,030 cP
PACM	28.7%	99.0%	20% in n-Octanol	Sl. Hazy Solution

The PACM-dimer acid composition #0014-104-A was surprisingly hard and brittle for a resin with a low SP (95°C). A composition similar containing a small amount of SCDA should boost the SP significantly, but it did not. Other than an increase in the weight of the diamine in the composition due to the higher MW of the diamine, the PACM-adipic acid polyamide #0014-116-A resembles

the formulation of the benchmark resin. It did not, however, have adequate solubility in n-octanol and retained a low SP. We will test the performance properties of resin #0014-104-A resin despite its low SP.

1,2-Diamino Cyclohexane (DACH)

#0014-116-B	Weight %	Equivalent %	Acid Number	11.2
Unitol BKS	19.3%	20.0%	Amine Number	8.3
Unidyme 14	56.1%	57.8%	Softening Point	151.8
Adipic Acid	5.5%	22.2%	Viscosity,175°C	127 cP
DACH	19.1%	99.3%	20% in n-Octanol	Soluble

#0018-61-B	Weight %	Equivalent %	Acid Number	5.2
Unitol BKS	18.4%	20.0%	Amine Number	3.7
Unidyme 14	60.1%	65.0%	Softening Point	116.5
Adipic Acid	3.5%	15.0%	Viscosity,150°C	572 cP
DACH	18.0%	98.0%	20%, Ethyl Lactate	Soluble

Previous work by Rumack demonstrated that this cyclic diamine increases the solubility of polyamides in non-hydroxylic solvents such as toluene and resulted in US #4,816,549 (1989). It imparts a lower softening point and more tack than EDA, so candidate polyamide #0014-116-A contains about twice the SCDA level than the benchmark. It is somewhat flexible, has a high SP, and dissolves in n-octanol, making it a promising candidate for further testing. However, this batch had both high acid and amine numbers and is perhaps a little richer in SCDA than it needs to be.

So I prepared a second batch, #0018-61-B to a lower acid number and amine number. It is soluble in ethyl lactate (and, presumable, n-octanol) and forms a clear gel in cyclohexanone. Although it is slightly tacky, it is somewhat flexible and should be a good candidate for further testing.

2-(2-Aminoethoxy)-1-Aminoethane (XTJ-504)

#0018-52-A	Weight %	Equivalent %	Acid Number	3.7
Unitol BKS	20.8%	20.0%	Amine Number	0.4
Unidyme 14	41.9%	40.0%	Softening Point	145.8
Adipic Acid	11.7%	40.0%	Viscosity,150°C	n.d.
XTJ-504	26.7%	99.0%	20% in n-Octanol	Hazy Gel

0014-128-B	Weight %	Equivalent %	Acid Number	
Unitol BKS	19.7%	20.0%	Amine Number	
Unidyme 14	53.8%	54.3%	Softening Point	149.3
Sebacic Acid	8.9%	25.7%	Viscosity,175°C	
XTJ-504	12.5%	49.1%	20% in n-Octanol	
EDA	5.1%	49.1%		

Huntsman XTJ-504 (formerly EDR-148) is an analog of HMDA, with an oxygen atom in place of a methylene group in the middle of the molecule. Dimer acid/adipic polyamide made with XTJ-504 as the only diamine(resin #0018-52-A) has an adequate SP but is slightly greasy, hazy and soft and does not form a clear solution in n-octanol.
Since it is an analog of HMDA, I also tried using it as I did HMDA in resin #0014-123-A, in a 1:1 admixture with EDA and reacted with a mixture of 2:1 equivalents dimer acid and sebacic acid.

Resin #0014-128-B is not promising despite a high (149°C) SP - it is flexible but weak (tears), is soft, slightly greasy, and slightly hazy. Although it dissolves in n-octanol, it does not have the feel of a serious resin candidate.

meta-Xylene Diamine (XDA)

#0014-107-A	Weight %	Equivalent %	Acid Number	21.1
Unitol BKS	23.1%	20.0%	Amine Number	0.3
Unidyme 14	34.9%	30.0%	Softening Point	189.3
Adipic Acid	14.8%	50.0%	Viscosity,150°C	n.d.
XDA	27.2%	99.0%	20% in n-Octanol	Hard,Hazy Gel

#0018-60-B	Weight %	Equivalent %	Acid Number	n.d.
Unitol BKS	21.0%	20.0%	Amine Number	n.d.
Unidyme 14	42.3%	40.0%	Softening Point	n.d.
Adipic Acid	10.7%	40.0%	Viscosity,150°C	n.d.
XDA	25.9%	103.0%	20% in n-Octanol	n.d.

#0018-57-A	Weight %	Equivalent %	Acid Number	2.4
Propionic Acid	9.1%	19.6%	Amine Number	3.6
Azeleic Acid	48.0%	80.4%	Softening Point	167.6
XDA	42.9%	100.2%	20% in n-Octanol	Opaque Solid

XDA is a "softer" diamine than DACH. Polyamides containing DACH as the sole diamine are very sticky. To prepare a candidate for this study, I first used a high adipic level (34%) which yielded a clear, somewhat tough material with a high SP (189). It was, however, insoluble in n-octanol. Two attempts to prepare a resin with less adipic acid such as #0018-60-B failed because the mixture developed insoluble white salt lumps.

To avoid this problem, I tried a dimer acid-free composition, #0018-57-A. It turned out clear, very hard, non-tacky and brittle. Unfortunately, it is insoluble in octanol. I made no further attempts with this diamine.

Bis(aminopropyl) Piperazine (BAPP)

#0018-54-A	Weight %	Equivalent %	Acid Number	4.0
Propionic Acid	5.7%	20.0%	Amine Number	224
Unidyme 14	44.6%	40.0%	Softening Point	169.5
Adipic Acid	11.3%	40.0%	Viscosity,200°C	281
BAPP	38.3%	98.9%	20% in n-Octanol	Soluble

#0018-57-C	Weight %	Equivalent %	Acid Number	4.5
Propionic Acid	7.8%	20.0%	Amine Number	n.d.
Azeleic Acid	40.0%	80.0%	Softening Point	163.5
BAPP	52.2%	98.9%	Viscosity,150°C	n.d
			20%, n-Octanol	Opaque Gel

BAPP introduces tertiary amine groups into the polyamide backbone, hence the high residual amine number. This feature is unique and may impart desirable adhesion and solubility charac-

teristics to the resin. Resin #0018-54-A is, for example, soluble in n-octanol and ethyl lactate. It is also brown in color and hazy, an indication of extensive crystallization of the BAPP-adipic acid chain segments. Despite these drawbacks, it is worth testing further.

The dimer acid-free resin #0018-57-C, which was hard and brittle, did not circumvent these problems and was less soluble in octanol but freely soluble in propionic acid.

Isophorone Diamine (IPDA)

#0018-51-B	Weight %	Equivalent %	Acid Number	8.6
Unitol BKS	26.3%	20.0%	Amine Number	2.2
Unidyme 14	10.6%	8.0%	Softening Point	124.0
Adipic Acid	24.2%	72.0%	Viscosity,175°C	1956 cP
IPDA	38.8%	99.0%	20%, Ethyl Lactate	Soluble

IPDA is the principal diamine component of UNI-REZ®150, a recently discontinued European ink resin. Because it is freely soluble in ethanol, we sampled it to Markem Corporation late in 2000 for an unknown digital ink application, where it received favorable interest. The candidate resin #0018-51-B differs from UR-150 in containing BKS fatty acid instead of stearic acid as terminator and a low level of dimer acid, which together lowered its SP to 124°C from that of UR-150 (177°C). Nevertheless, this resin is clear, hard, brittle and alcohol-soluble; a good candidate.

Trimethylhexamethylene Diamine (TMHMDA)

#0014-87	Weight %	Equivalent %	Acid Number	n.d.
Propionic Acid	6.6%	14.2%	Amine Number	n.d.
Sebacic Acid	54.4%	85.8%	Softening Point	176.0
TMHMDA	33.1%	66.5%	Viscosity,150°C	n.d.
EDA	6.0%	31.6%	20% in n-Octanol	Cloudy Gel

#0018-57-B	Weight %	Equivalent %	Acid Number	n.d.
BKS	29.4%	19.9%	Amine Number	n.d.
Adipic Acid	30.2%	80.1%	Softening Point	67.3
TMHMDA	40.4%	98.7%	Viscosity,150°C	n.d.
			20% in n-Octanol	n.d.

#0018-61-A	Weight %	Equivalent %	Acid Number	8.5
BKS	21.6%	20.0%	Amine Number	0.6
Unidyme 14	32.4%	30.0%	Softening Point	80.2
CHDA	16.2%	50.0%	Viscosity,150°C	n.d.
TMHMDA	29.7%	99.6%	20%, Ethyl Lactate	Soluble

#0018-62-B	Weight %	Equivalent %	Acid Number	7.5
BKS	23.3%	20.0%	Amine Number	0.4
Unidyme 14	23.5%	20.0%	Softening Point	91.4
CHDA	21.1%	60.0%	Viscosity,150°C	2300 cP
TMHMDA	32.1%	99.4%	20%, Ethyl Lactate	Soluble

Like IPDA, TMHMDA imparts amorphous but tacky character to a polyamide. The polyamide of TMHMDA and adipic acid is, in contrast to that of IPDA, too soft and sticky to be useful.

In order to reduce tack and increase SP, I tried two different types of compositions. I first used a significant level of EDA as co-diamine in a dimer acid-free composition with sebacic acid. This rendered the resin insoluble in n-octanol.

I then prepared mixed dimer acid/1,4-CHDA composition, #0018-61-A. 1,4-CHDA usually forms intractable salts with diamines (other than dimer diamine and some alkyleneoxy diamines, see below) but cooked well with TMHMDA. Resin #0018-61-A was surprisingly low in SP (80°C), yet was hard, flexible-brittle, only slightly tacky, and soluble in ethyl lactate. Resin #0018-62-B contains more CHDA. Consequently it has a higher SP (91°C), is hard, tack-free and slightly tough. It is a candidate for further testing.

Poly(alkyleneoxy) Diamine (Jeffamines D-2000, XTJ-500, D-400 and D-230)

0014-55-A	Weight %	Equivalent %	Acid Number	1.5
Propionic Acid	0.7%	10.0%	Amine Number	0.2
1,4-CHDA	7.5%	90.0%	Softening Point	52.0
D-2000	91.8%	94.6%	Viscosity,140°C	1,630 cP
			20% in n-Octanol	Soluble

0014-83-B	Weight %	Equivalent %	Acid Number	8.0
BKS	16.8%	20.0%	Amine Number	0.8
1,4-CHDA	20.2%	80.0%	Softening Point	107.0
D-400	63.1%	97.8%	Viscosity,140°C	167 cP
			20% in n-Octanol	Soluble

0014-118-B	Weight %	Equivalent %	Acid Number	9.0
BKS	17.9%	20.0%	Amine Number	2.4
1,4-CHDA	21.6%	80.0%	Softening Point	148
D-400	51.4%	74.6%	Viscosity,175°C	61 cP
D-230	9.2%	24.4%	20% in n-Octanol	Clear Gel

Poly(alkyleneoxy) diamines, available in a number of molecular weights and types from Huntsman and BASF, are "soft" diamines since they contain ether groups which impart chain flexibility or

mobility to polyamides made with them, lowering softening points and decreasing crystallinity. The ether linkage also makes these polyamides more compatible with polar solvents. The larger the PAO segment of the diamine, the greater its weight % contribution to the formulation and the larger the influence the PAO diamine exerts on physical properties.

For example, the reaction products of Jeffamines D-2000 and XTJ-500 with any diacid other than 1,4-CHDA are probably viscous oils. The CHDA/D-2000 polyamide, resin #0014-55-A (10% terminated), has a SP of 52°C. These polyamides have desirable solubility in glycol ethers and diesters but are too soft and sticky to be serious ink resin candidates.

For our program, then, only the lower molecular weight PAO diamines will serve. We prepared a number of polyamides using Jeffamine D-400 and terminated either with Unitol BKS fatty acid or propionic acid. The CHDA/D-400 polyamide #0014-83-B is promising, with a SP of 107°C, but it is soft and tears easily.

I tried to increase hardness with a material made with D-400 and D-230, a diamine which increased the SP to 148°C range (#0014-118-B). This material, however, is still soft and it lost some solvent compatibility, forming a gel in n-octanol. We will take it on for further testing anyway.

<u>Versamine 551 Dimer Diamine</u> (V551)

0018-49-B	Weight %	Equivalent %	Acid Number	1.7
Propionic Acid	4.0%	20.0%	Amine Number	5.7
1,4-CHDA	18.5%	80.0%	Softening Point	160.0
V551	77.5%	101.2%	Viscosity,150°C	n.d.
			20% in n-Octanol	Clear Gel

0018-56-B	Weight %	Equivalent %	Acid Number	9.3
Propionic Acid	5.7%	20.0%	Amine Number	0.2
1,4-CHDA	26.3%	80.0%	Softening Point	132.0
V551	54.3%	50.0%	Viscosity,175°C	426 cP
Cyclohexanedimethanol	13.7%	50.0%	20% in n-Octanol	Soluble, with sl. haze

Like the Jeffamine PAO diamines, dimer diamine is a "soft" or amorphous material. I expected to be able to make a solid polymer using only the hardest diacids. In fact, the CHDA polyamide is a very promising material, high in SP, clear, tack-free, and flexible. Unfortunately, it lacks solubility in n-octanol.

To improve solubility of this type of resin, I introduced ester linkages into the backbone. Resin #0018-56-B is a poly(ester-amide) with unusual and promising properties. It is clear, quite flexible without brittleness, light-colored and tack-free. Although it is not perfectly soluble in n-octanol and forms a cloudy gel in ethyl lactate, it exhibits some hydrocarbon compatibility. For example, it dissolves in a mixture of 4:1 limonene:octanol and in a 3:1 mixture of limonene:ethyl lactate (but not limonene itself) and forms a clear gel in a 1:1 mixture of cyclohexanone and decalin. Of all of the resins in this report, this one is the most interesting as an ink resin candidate.

CONCLUSION

The following resins, the most promising polyamides from the above screening study, will be tested further for performance properties.

#0014-123-A	Weight %	Equivalent %
Unitol BKS	18.2%	20.0%
Unidyme 14	65.3%	71.4%
Sebacic Acid	2.8%	8.6%
HMDA	4.7%	49.1%
EDA	9.1%	49.1%

#0014-104-A	Weight %	Equivalent %
Unitol BKS	14.6%	20.0%
Unidyme 14	58.8%	80.0%
PACM	26.6%	99.0%

#0018-61-B	Weight %	Equivalent %
Unitol BKS	18.4%	20.0%
Unidyme 14	60.1%	65.0%
Adipic Acid	3.5%	15.0%
DACH	18.0%	98.0%

#0018-54-A	Weight %	Equivalent %
Propionic Acid	5.7%	20.0%
Unidyme 14	44.6%	40.0%
Adipic Acid	11.3%	40.0%
BAPP	38.3%	98.9%

#0018-51-B	Weight %	Equivalent %
Unitol BKS	26.3%	20.0%
Unidyme 14	10.6%	8.0%
Adipic Acid	24.2%	72.0%
IPDA	38.8%	99.0%

#0018-62-B	Weight %	Equivalent %
BKS	23.3%	20.0%
Unidyme 14	23.5%	20.0%
CHDA	21.1%	60.0%
TMHMDA	32.1%	99.4%

0014-118-B	Weight %	Equivalent %
BKS	17.9%	20.0%
1,4-CHDA	21.6%	80.0%
D-400	51.4%	74.6%
D-230	9.2%	24.4%

0018-56-B	Weight %	Equivalent %
Propionic Acid	5.7%	20.0%
1,4-CHDA	26.3%	80.0%
V551	54.3%	50.0%
Cyclohexanedimethanol	13.7%	50.0%